Use of Gradient Dilution to Flag and Overcome Matrix Interferences in Axial-Viewing Inductively Coupled Plasma-Atomic Emission Spectrometry

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Abstract

Despite the undisputed power of inductively coupled plasma-atomic emission spectrometry (ICP-AES), its users still face serious challenges in obtaining accurate analytical results. Matrix interference is perhaps the most important such challenge. Dilution of a matrix-containing sample is a common practice to reduce matrix interference. However, determining the optimal dilution factor requires tedious and time-consuming offline sample preparation, since emission lines and the effect of matrix interferences are affected differently by the dilution. The current study exploits this difference by employing a high-performance liquid chromatography gradient pump prior to the nebulizer to perform on-line mixing of a sample solution and diluent. Linear gradient dilution is performed on both the calibration standard and the matrix-containing sample. By ratioing the signals from two emission lines (from the same or different elements) as a function of dilution factor, the analyst can not only identify the presence of a matrix interference, but also determine the optimal dilution factor needed to overcome the interference. A ratio that does not change with dilution signals the absence of a matrix interference, whereas a changing ratio indicates the presence of an interference. The point on the dilution profile where the ratio

stabilizes indicates the optimal dilution factor to correct the interference. The current study was performed on axial-viewing ICP-AES with *o*-xylene as the solvent.

Keywords: Inductively Coupled Plasma Atomic Emission Spectrometry; Organic solvents; Gradient dilution; Matrix effects; Axial viewing

1. Introduction

Identification and remediation of non-spectral interferences remains a critical challenge in inductively coupled plasma-atomic emission spectrometry (ICP-AES) [1]. Without knowledge of the composition of a sample solution, which itself is the subject of the analysis, matrix interferences are difficult to detect or correct. Since awareness of the existence of a problem is the first step towards its correction, it is desirable to have indicators that can alert an operator of the presence of matrix effects in an on-line fashion. Potential indicators were previously examined by our research group [2]. Among the possible methods, we concluded that monitoring argon emission and spatially resolved analyte emission was attractive for flagging plasma-related matrix effects. Both indicators exploited changes in emission signals to flag effects caused by a sample matrix. A similar principle is employed in the present study to flag and correct matrix interferences.

Of similar importance to recognition of matrix effects is their correction. Four of the most commonly used methods to control matrix effects are matrix stripping, matrix matching, internal standardization, and standard additions [3-6]. Unfortunately, each of these methods carries inherent limitations. Matrix stripping is often not fully effective and can result in loss of analyte. Similarly, matrix matching requires prior knowledge or analysis of the sample composition in order to provide an accurate match to the sample matrix. Apart from matrix-

manipulation methods, internal standardization requires that added standards be carefully chosen to ensure similar signal response between the standards and analytes. In addition, more than one internal standard might be needed for a multi-element analysis, which increases complexity and can itself result in additional inter-element effects. The same holds true for the standard-addition method. The number of added standards must at least equal the number of analytes. The concentrations of the standard-addition solutions also play an important role. Inaccurate results can arise if the standard-addition concentrations are too high or too low compared to the analyte. Studies [7] have shown that the concentration ratio of an added standard and sample should be at least two to ensure adequate precision and accuracy. Pre-analysis of the sample is therefore needed to obtain a rough estimate of the analyte concentration. In addition, too high of an added concentration can significantly alter the matrix composition of the sample, especially when multi-additions are needed. Last of all, these four methods all require the addition of foreign reagents to the sample solution, which increases the likelihood of contamination.

Considerable work has been done to alleviate the drawbacks of traditional methods. To shorten sample preparation and analysis time, and to reduce human error and chemical impurities, high-performance liquid chromatography (HPLC) pumps, multi-peristaltic-pump systems, and flow injections have been used to mix standards and analyte solutions on-line. These approaches were used with atomic absorption [8-10], atomic emission [11], and mass spectrometry [12-14]. However, a major limitation of these methods was the time lag between successive gradient steps and the limited gradient resolution of HPLC pumps. To avoid the addition of foreign reagents, Al-Ammar and Barnes [6] developed an internal standardization method to correct matrix interference by relating the ratios of two spectral-line intensities of the same analyte and matrix concentration. Despite the effectiveness of this method, pre-determination of the matrix

concentration and the correction factors are still required. Dilution of the matrix is also commonly used to reduce the magnitude of a matrix effect [5], since the matrix concentration is often directly proportional to the magnitude of the matrix effect [4, 15]. Unfortunately, analysis of discrete dilutions is required to obtain a suitable dilution factor where the matrix effects are reduced to an acceptable level. Such analyses are tedious and time-consuming, given the offline sample preparation that is required.

The present study explores an improved sample introduction system that overcomes the drawbacks associated with typical dilution analysis and offers higher accuracy. This method enables both on-line identification and remediation of non-spectral matrix interferences. The method employs a gradient high-performance liquid chromatography (HPLC) pump to perform on-line dilution of a sample solution. Small gradient steps were performed during the analysis and no time lag between steps was observed. Furthermore, the accuracy of the gradient pump was found to be better than 1% with organic-solvent-based ICP analysis, which agrees with the results of a recent study [16] that employed the same pump to perform standard-addition experiments.

Measurement of the intensity ratio of two emission lines (from the same or different elements) as a function of dilution enables detection of the presence of matrix interferences. A constant emission-intensity ratio is observed for samples free of matrix interference. In contrast, for a sample that suffers from interferences, the intensity ratio will change with dilution, as a result of concentration-dependent differences in the effect of the matrix on emission lines with different upper-state energies. A suitable dilution factor to overcome the interference can then be identified as the point on the dilution-dependent intensity-ratio profile where the ratio reaches a constant value. Conveniently, use of a linear gradient dilution enables the time dependence of

the ratio to be used directly. The sample can then be diluted on-line and analyzed at a concentration where it is free of the matrix interferences.

Axial-viewing ICP-AES is employed in the current study with *o*-xylene as solvent. The axial-viewing mode offers better detection limits than conventional radial viewing, but is known to be even more prone to matrix effects [17, 18]. Organic-solvent based analysis is widely used in the petroleum, pharmaceutical, food and other industries since the wide variety of chemical and physical properties of organic solvents enable dissolution of compounds and liquids beyond those offered with aqueous matrices. Unfortunately, the different chemical and physical properties of organic solvents make these analyses more susceptible to sample-introduction-related matrix interference. Further, plasma-related matrix interferences have been reported in organic-solvent-based ICP analyses and are still not well understood [19]. Accordingly, it is particularly attractive to explore methods to flag and overcome matrix interference in such analytical settings.

2. Experimental

2.1. Instrumentation

The gradient-dilution system is similar to one described earlier [16]. A gradient HPLC pump (Hitachi Ltd. Model L-7100 pump) was used both to perform on-line mixing of samples and to introduce the resulting solutions into the nebulizer. This pump offers a range of mixing ratios from 0–100% in increments of 1%. Both discrete and gradient mixing can be performed, although the present study employed only linear gradients. A flow restrictor (PEEK polymer capillary tubing of 0.08 mm I.D.) was installed at the outlet of the gradient pump to increase pump backpressure and thereby to improve flow stability. Solutions exiting the flow restrictor were directed into a Meinhard nebulizer, and the resultant spray passed through a chilled (5°C),

water-jacketed Scott-type double-pass spray chamber prior to introduction into the ICP. A Thermo Finnigan Element ICP torch with a 1.5 mm (I.D.) injector tube was used in all experiments.

Unless otherwise specified, the ICP operating parameters used in all experiments were as listed in Table 1. A commercial ICP–AES Czerny-Turner spectrometer (Horiba Jobin-Yvon ACTIVA ICP–AES spectrometer, Longjumeau, France) was used. This spectrometer employs a two-dimensional CCD detector that can simultaneously collect spatially resolved emission signals across the entire cross section of the plasma in the axial-viewing mode [20, 21], as well as multiple emission lines within a selected spectral window (4 nm to 8 nm, depending upon the grating being used).

2.2. Reagents and solvents

Multielement solutions were prepared by diluting certified standards (Conostan custom blend, division of SCP Science, Baie D'Urfe, Canada) in *o*-xylene. Reference solutions contained only the analytes in 100% *o*-xylene. For plasma-related matrix-effect experiments, the *o*-xylene solutions contained the same analyte concentrations as the reference solutions, but also contained a few hundred ppm of selected matrix elements. For sample-introduction-related matrix-effect experiments, solutions contained the same concentration of analytes as reference solutions but were dissolved in a 10% toluene, 90% *o*-xylene solvent.

2.3. Experimental procedures

Signals from emission lines of two analytes (or of the same analyte) were collected simultaneously while the matrix-free solution was diluted in a linear gradient. The same exercise was repeated with the matrix-containing sample solution. The intensity ratios of the two lines for

both the matrix-free and matrix-containing conditions were then plotted against time. Because linear dilution gradients were used, time on these plots is proportional to dilution factor, in accordance with Equation (1).

$$\text{Dilution Factor (DF)} = \frac{\text{Total analysis time (T)}}{\text{Total analysis time (T)} - \text{Time of data collection (t)}} \quad (1)$$

In the absence of a matrix interference, the intensity ratio of the two emission lines will be consistent throughout the gradient dilution, as long as the analyte itself does not appreciably alter the ICP conditions. However, if a matrix interference is present, the signal of one emission line will often differ from that of other emission lines as dilution proceeds, because of the concentration-dependent effect of the matrix on the ICP. In this case, the intensity ratio will vary with dilution. One reason for this behavior is the difference in the matrix effect on lines of different upper-state energies. The dilution-dependent change in intensity ratio can then be used as an indicator for the presence of a matrix interference.

Of course, it is essential to define a parameter to identify whether the intensity-ratio change is statistically meaningful. In the present study, this statistical test is applied to the “flatness” of the gradient line-intensity-ratio profile. In turn, this “flatness” is expressed as “relative range” [2], which refers to the range of all data points (line-intensity ratios) divided by the mean, and expressed as a percentage. To avoid distortion from outliers, only the range from 5% to 95% of the data points was used. The first step is to employ a matrix-free calibration standard to establish a “flatness threshold”, since for some elements the analyte itself might alter the line ratio during dilution. The existence of a matrix effect in a real sample can then be flagged if the ratio exceeds the pre-determined flatness threshold.

3. Results and discussion

3.1. Detecting matrix interference

In the current study, two pairs of emission lines and two types of non-spectral interferences were investigated. Emission lines of Zn I (213.86 nm) and Cu I (213.60 nm) were chosen because of their wavelength proximity and the difference in their upper-state energies. Two spectral lines of magnesium (Mg I 285.21 nm and Mg II 280.27 nm) were chosen not only because of differences in their upper-state energies, but also for use of the Mg ionic-to-atomic line intensity ratio to monitor plasma conditions [22]. The relative range for the matrix-free solutions and a drift test was found to be approximately 7% for the intensity ratio of both the Zn I 213.86/Cu I 213.6 and Mg II 280.27/Mg I 285.21 line pairs. Any intensity-ratio dilution profile having a curvature greater than the defined flatness threshold (relative range) of 7% can be classified as being influenced by a matrix effect.

There exist two types of non-spectral matrix interferences—plasma-related and sample-introduction related. Plasma-related matrix interferences are caused by sample constituents that lead to changes in either or both the excitation and ionization conditions of the plasma. The analytical signal can be enhanced or depressed, depending on how plasma conditions are altered. Potassium was chosen as the matrix element for the plasma-related matrix interference study due to its historical reputation as one of the easily ionized elements that cause a plasma-related matrix interference [23, 24]. Figures 1a and 1b show gradient-dilution profiles of the Zn I 213.86 nm and Cu I 213.60 nm lines in the absence (red trace) and presence (black trace) of a plasma-related matrix interference. In this case, the matrix-free solution was prepared in 100% *o*-xylene while the matrix-containing solution had 400 ppm K added. From these two plots, an emission enhancement occurred at the beginning of the gradient dilution, with the enhancement more

pronounced for Zn than Cu. As sample dilution proceeds, the enhancement declines until the emission intensity becomes comparable to that of the matrix-free solution.

Figure 2 displays the intensity ratio of the Zn and Cu emission lines throughout the course of the dilution. As before, the red trace corresponds to the intensity ratio of the matrix-free solution while the black trace pertains to the matrix-containing solution. At the end of each set of experiments, a drift test (blue trace) was performed by a second analysis of the matrix-free solution. This test confirmed that any signal changes during the experiment were induced by the matrix rather than by system drift. The remaining (green) trace exhibits a Zn/Cu line ratio for a later experiment that investigated sample-introduction-related matrix effects, described later. In Figure 2, a changing ratio profile is observed for the solution with the K matrix. The strong dilution dependence of the Zn/Cu ratio greatly exceeds the “flatness threshold” defined by the reference (7% in this case), so the method successfully flags the presence of the matrix effect induced by K.

Sample-introduction-related matrix interferences are caused by differences in physical properties (e.g., viscosity, density, surface tension) between the sample and standard solutions, which lead to changes in aerosol-droplet formation and transport into the plasma. In this experiment, a reference solution was prepared in 100% *o*-xylene while the matrix-containing solution was in 10% toluene and 90% *o*-xylene, both with the same concentration of analytes. Toluene was chosen due to its higher volatility than *o*-xylene and also because it is a commonly used solvent in ICP analysis of organic samples.

Figures 3a and 3b show the time (dilution)-dependent intensity profiles of the Mg I 285.21 nm and Mg II 280.27 nm lines. Signal depression was observed for both emission lines in the presence of toluene. Figure 4 shows the time (dilution)-dependent ratio profiles for these

two emission lines in the presence and absence of both K and toluene matrices. As in the case of the Zn/Cu line pair (cf. Fig. 2), significant dilution-dependent ratios (exceeding the defined relative-range “flatness”) were observed for the Mg II/Mg I line pair in the presence of a 400 ppm K matrix, which leveled off at a similar dilution as in the Zn/Cu experiment. In contrast, the toluene matrix exerted a much smaller effect; although a clear signal suppression occurred in the presence of the added toluene (cf. Fig. 3), the two Mg lines were affected similarly, so the ratio profile is relatively flat (cf. Fig. 4). The same lack of sensitivity to solvent composition is apparent for the Zn/Cu line pair (cf. Fig. 2, green trace). Clearly, the gradient-dilution method fails to flag this sample-introduction-related matrix effect. This result is not surprising, since the effect of a change in solvent serves mainly to alter the amount of sample material that reaches the plasma and not the excitation or ionization conditions in the discharge. The slight drop-off in all of the profiles in Figure 4 at later times might be due to the low sample concentration as the dilution increased, and the resulting increase in relative noise. Regardless of the reason for this drop-off, the dilution at these later times is so large that the region is of little analytical utility.

Mg ionic-to-atomic intensity ratios are often used to evaluate plasma conditions (i.e. robustness) [22]. From Figure 4, plasma conditions can also be exploited to evaluate an observed matrix interference. Low Mg II/Mg I ratios indicate degraded plasma robustness at high K matrix concentration. This ratio rises and approaches a constant, high value as the matrix concentration is diluted. However, in the presence of toluene, the interference is caused by differences in droplet formation and transport. Plasma robustness is not affected significantly, as indicated by the relatively high and constant Mg II/Mg I ratio.

3.2. Determining optimal dilution factor

The dilution factor needed to reduce matrix effects to an acceptable level can be identified as the point on plots such as Figures 2 and 4 where the signal ratio becomes virtually constant (i.e. comparable to that of the matrix-free sample and the drift test). Figures 5a and 5b are an expanded version of Figures 2 and 4 with the x-axis converted to the proportional dilution factor. The yellow triangles in Figures 5a and 5b indicate where the profiles become flat, with relative ranges similar to that of the matrix-free sample. This point indicates the dilution factor needed to limit matrix interference without suffering significant sensitivity loss from dilution. Figures 5a and 5b exhibit similar optimal dilution factors (about 1.45), which underscore the effectiveness of the method and how little signal loss is incurred.

To confirm experimentally that the dilution factors determined from Figures. 5a and 5b are effective, the original K-containing sample solution was manually diluted by a factor of 1.45 and analyzed. Calibration curves for this analysis were developed for the Zn I 213.86 nm and Cu II 213.60 nm from matrix-free standard solutions (with r^2 values of 0.9990 and 0.9992 respectively). The errors between the true and calculated concentrations were about 0.04% to 3.06% (five replicates for each emission line), well within the noise level of 7% (the flatness threshold adopted here).

4. Conclusions

The dilution-dependent intensity-ratio profiles of two emission lines, produced by gradient dilution, can be used to flag plasma-related matrix interferences (K matrix in the current study). Statistically significant changes in the ratio are identified by comparison of the “relative range” of a sample to that of a matrix-free (standard) solution. However, sample-introduction-related matrix effects cannot be flagged by the intensity-ratio profiles due to their small effect on plasma conditions.

The optimal dilution factor to bring a matrix interference within an acceptable level can be determined as the point where the dilution-dependent ratio profile becomes virtually constant. In the case of a linear gradient dilution, the time axis can easily be converted to dilution factor directly. Analysis of a matrix-containing sample that has been manually diluted to the optimal level demonstrates the effectiveness of the method.

In the future, this study will be expanded to include aqueous solutions and radial viewing in ICP-AES. It will also be explored as a means to flag and overcome matrix interferences in ICP-mass spectrometry.

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Table 1. Instrument operating parameters

ICP Spectrometer	Horiba Jobin-Yvon ACTIVA	Sample uptake rate	0.35 mL/min
Forward power	1300 W	Plasma axial cutoff gas flow (nitrogen)	25 L/min
Outer gas flow (argon)	14 L/min	Central channel Oxygen flow	10 mL/min
Intermediate gas flow (argon)	1.2 L/min	Sheath gas flow (argon)	0.1 L/min
Nebulizer gas flow (argon)	0.35 L/min	Spray Chamber Temperature	5 °C

Figure 1. Time (dilution)-dependent intensity profiles of (a) Zn I 213.86 nm, (b) Cu II 213.60 nm in the absence (red trace) and presence (black trace) of a 400 ppm K matrix.

Figure 2. Time (dilution)-dependent ratio profiles of Zn/Cu in the absence of a matrix (red trace), and the presence of 400 ppm K (black trace) and 10% v/v toluene (green trace) matrices. The drift test (blue trace) indicates there was no significant instrumentation drift during this trial.

Figure 3. Time (dilution)-dependent intensity profiles of (a) Mg I 285.21 nm and (b) Mg II 280.27 nm emission in the absence (red trace) and presence (green trace) of 10% toluene as a matrix.

Figure 4. Time (dilution)-dependent ratio profiles of the Mg II/Mg I emission line pair in the absence (red trace) and presence of K (black trace) and toluene (green trace) matrices. The drift test (blue trace) indicates there was no significant instrumental drift during this trial.

Figure 5. Intensity-ratio dilution profiles of (a) Zn/Cu and (b) Mg II/Mg I emission line pairs as a function of dilution factor. The yellow triangles indicate the optimal dilution factor for each analysis, at which the matrix interference is minimized.

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